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(54) ## Novel water-absorptive composite material and method for the preparation thereof.

(57) A water-absorptive and biodegradable composite material capable of being shaped into a form of, for example, film or sheet is prepared by blending 100 parts by weight of finely beaten cellulose pulp, 5 to 100 parts by weight of a chitosan salt, e.g., acetate, and 10 to 300 parts by weight of glutinized starch in the form of an aqueous slurry and sheet-making the slurry followed by a heat treatment at to 200 °C. The composite material is water-absorptive and biodegradable but has a high strength even in water so that it is useful, for example, as a sanitary absorbent material which is disposable without the problem of environmental pollution due to the decomposition products.

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NOVEL WATER-ABSORPTIVE COMPOSITE MATERIAL AND METHOD FOR THE PREPARATION THEREOF

The present invention relates to a novel composite material in the form of a shaped body having water-absorptivity but free from disintegration in water. More particularly, the present invention relates to a shaped body of a composite material basically formed of cellulose fibers and chitosan and having biodegradability, for example, in soil. The invention also relates to a method for the preparation of such a composite material.

The composite material of the invention is useful in a wide variety of applications, mainly but not limitatively, in the form of a sheet used, for example, as a sanitary absorbent material, sheet material for agricultural uses, temporary pots for growing young garden trees and seedlings and the like. The services expected for the sheet materials in the above mentioned applications are mostly of a temporary nature so that it is desirable that the sheet material can be spontaneously decomposed after use or after lapse of the service season without leaving any decomposition products which may cause a problem in environmental pollution.

The most serious problem in the widely prevailing applications of synthetic resin- and fiber-made articles is that synthetic resin in general is highly resistant to attack from microorganisms so that debris of the articles remain in the soil or in water semipermanently so as to cause a problem of environmental pollution as a counterpart of the advantageous durability of the articles. Incineration treatment as a means of waste disposal is also not free from some problems when waste materials are synthetic resin-made. In view of these problems, it is highly and eagerly desired to develop a polymeric material suitable for shaping of various articles having moderate durability but capable of being rapidly decomposed microbiologically when the article has finished its service without causing problems in environmental pollution.

Many of the naturally occurring polymeric materials of botanical origin such as cellulosic pulp as a typical carbohydrate polymer may meet the above mentioned requirements of biodegradability to some extent. Cellulosic materials, however, have a limitation in respect of the shaping method applicable thereto and it is a difficult matter to prepare a precision-shaped article from a cellulosic material. Moreover, an article shaped from a cellulosic material is defective in respect of durability and stability, in particular, in water. Starch is another typical carbohydrate polymer but is highly swellable in water so that a shaped body made from starch is readily disintegrated in water unless the shaped article is subjected to a crosslinking treatment by using formaldehyde and the like as a crosslinking agent while even a trace amount of formaldehyde remaining in the shaped articles may cause a serious problem to human health.

It is known, on the other hand, that some naturally occurring polymeric materials of animal origin can be used as a material of shaped articles including, for example, chitosan. A problem in the use of chitosan is that, while chitosan is obtained in the form of a salt, chitosan salts cannot be shaped, for example, into films by mere drying without the troublesome procedure of fixing by an alkali treatment.

Two of the inventors have previously proposed a biodegradable composite polymeric material made from cellulosic fibers and chitosan. The polymer proposed, however, is poorly water-absorptive so that it is also desirable to impart such a biodegradable composite material with increased water-absorptivity. for example, in application to sanitary absorbent materials.

An object of the present invention accordingly is to provide a shaped article of a novel biodegradable composite polymeric material from naturally occurring polymeric materials having adequate water-absorptivity yet not to cause disintegration in water though to be swellable to some extent.

Thus, the invention provides a novel shaped body of a water-absorptive and biodegradable polymeric composite material which comprises:

(A) 100 parts by weight of fine cellulose fibers;

(B) from 5 to 100 parts by weight of chitosan; and

(C) from 10 to 300 parts by weight of glutinized starch.

The above defined cellulose fiber-based water-absorptive and biodegradable polymeric composite material is prepared by a method which comprises the steps of:

(a) blending 100 parts by weight of fine cellulose fibers, an aqueous solution of a chitosan salt in an amount from 5 to 100 parts by weight as chitosan and from 10 to 300 parts by weight of glutinized starch to give an aqueous slurry;

(b) shaping the aqueous slurry of the compound into a form; and

(c) drying the thus shaped form of the compound by heating at a temperature in the range from 50 to 200 °C.

As is described above, the essential components in the inventive composite material include cellulose fibers, chitosan and glutinized starch. These materials are each a naturally occurring polymeric material and can be rapidly decomposed microbiologically in the soil or in water including sea water and river water

without the problem of environmental pollution due to decomposition products. When either one of these materials alone is shaped and dried into a shaped body, however, it can hardly be expected that such a shaped body retains the dry form or mechanical strength under a watery environment encountered in water or in moistened soil. This is also the case with shaped articles prepared from a combination of cellulose fibers and starch or a chitosan salt and starch. Although a composite material of cellulose fibers and a chitosan salt may have improved water resistance, such a composite material is poor in water absorptivity so that such a composite material cannot be used in applications where water-absorptivity of the material is desirable. On the contrary, it has been unexpectedly discovered that a ternary composite material of cellulose fibers, chitosan and glutinized starch has remarkably improved water absorptivity without substantial decrease in water resistance and retaining shape in water. The biodegradability of the inventive composite material can be controlled by suitably selecting the proportion of the components and the conditions for shaping.

The type of the cellulose fibers used as the component (A) in the inventive composite material is not particularly limitative including so-called lignocellulose, pectocellulose, bacteria cellulose and the like. It is important that the cellulose fibers have high fineness as imparted by any known method such as beating in a beater conventional in the paper making industry to have a specified Canadian standard freeness of, for example, 50 ml or less.

Starch as the component (B) of the inventive composite material is a carbohydrate polymer of low cost as obtained from various kinds of plants accumulating starch as a nutritive source. The type or origin of the starch is not particularly limitative including potato, Indian corn, wheat, rice and the like.

Chitosan as the component (C) in the inventive composite material is a nitrogen-containing polymeric material derived from chitinous material occurring in nature as a constituent of the shell of crustacean animals and certain fungal bodies. Specifically, chitosan is a deacetylation product of chitin with a relatively high degree of deacetylation. In the method of the present invention, it is desirable that the degree of deacetylation is at least 40% in order that the chitosan is soluble in an aqueous medium acidified, for example, with acetic acid forming an acetate.

In the preparation of the inventive composite material, 100 parts by weight of fine cellulose fibers are blended with 5 to 100 parts by weight of the chitosan salt, e.g., acetate, in the form of an aqueous solution and then admixed with an aqueous solution of glutinized starch prepared in advance by heating a dispersion of starch in water so as to give an aqueous slurry. The amount of the glutinized starch is in the range from 50 to 300 parts by weight per 100 parts by weight of the cellulose fibers. The above mentioned order of addition of the chitosan salt and the glutinized starch can of course be reversed. It is optional as required to mix the aqueous slurry with plasticizers, fillers, coloring agents and the like. The aqueous slurry of the essential and optional components are then shaped and dried and heat-treated at a temperature in the range from 50 to 200 °C so that the blend is converted into a composite material shaped in a desired form such as a sheet or film. The length of time for this heat treatment should not be excessively long so as to avoid yellowing, especially, when the temperature is relatively high. The thus obtained sheet or film of the invention is translucent and has adequate water absorptivity and biodegradability as well as sufficiently high dry and wet strength which can be controlled by selecting the amount of the chitosan and starch and the temperature of the heat treatment. The method for shaping the slurry into a form is not particularly limitative. When the desired form of the shaped article is a film or sheet, the well established technology in the paper-making process is applicable. It is a feature of the invention that, although each of the chitosan salt and glutinized starch is soluble in water, the composite shaped article prepared from these components and the cellulose fibers is no longer disintegrable in water, presumably, as a result of the heat treatment after shaping, by which the chitosan salt is at least partly converted into free chitosan.

In the following description, examples are given to illustrate the composite material of the invention and the method for the preparation thereof in more detail although the scope of the invention is not limited thereto in any way. In the following description, the term "parts" always refers to parts by weight".

Example 1.

An aqueous slurry was prepared by blending 100 parts of finely beaten bleached conifer pulp having a Canadian standard freeness of 10 ml or smaller with an aqueous solution of chitosan acetate derived from lobster shells in a varied amount of 1 to 100 parts as chitosan and an aqueous solution of glutinized potato starch in an amount of 50 parts as starch. The aqueous slurry contained 0.5% by weight of the cellulose fibers. The slurry was spread over a plastic-made dish and dried and heat-treated for about 15 hours in an air circulation oven at 70 °C so that a translucent film having a thickness of about 60 µm was obtained.

The thus prepared films of the composite material were subjected to measurement of dry and wet strength, absorption of water and evaluation of biodegradability to give the results shown in Table 1 below. The biodegradability was evaluated in an accelerated decomposition test by culturing chitosan-decomposing bacteria in the presence of the film to record the number of days taken until the film was finely disintegrated into pieces. The test of biodegradability was conducted as follows. Thus, three test pieces each 7 mm by 7 mm wide were taken in a test tube together with 5 ml of a standard liquid culture medium and a glass bead of 6 to 8 mesh fineness and, after inoculation of the culture medium with a cultured stock of a microorganism belonging to the genus of Pseudomonas isolated from a soil in Japan, the test tube was shaken at 28 °C until two of the three test pieces were disintegrated. In a rough estimation, a day in this acceleration test corresponds to 10 days of decomposition in soil though dependent on various parameters.

As is understood from the results shown in Table 1, the amount of the chitosan is a critical parameter for the wet strength of the film and a practically useful wet strength can be obtained only when the amount of the chitosan is 5% by weight or more based on the cellulose fibers.

Table 1

Chitosan, parts	1	5	10	50	100
Dry strength, kg/cm²	600	800	1000	1000	1000
Wet strength, kg/cm²	< 50	400	500	550	400
Water absorption, %	250	200	150	80	50
Biodegradability, days	< 1	2	3	4	20

Example 2.

The experimental procedure was substantially the same as in Example 1 in each of the experiments except that the amount of chitosan was always 20 parts and the amount of glutinized potato starch was varied in the range from 10 to 500 parts per 100 parts of the cellulose pulp. The results of the tests for dry and wet strength, the amount of water absorption and the biodegradability are shown in Table 2 below.

As is understood from the results shown in Table 2, the water absorptivity is greatly influenced by the amount of the starch and adequate water absorptivity is obtained when the amount of starch is 50 parts or more per 100 parts of the cellulose pulp while an excessively large amount of starch, e.g., 500 parts, is undesirable due to the great decrease, in particular, in the wet strength of the film.

Table 2

Potato starch, parts	10	50	100	300	500
Dry strength, kg/cm²	1100	1000	1000	450	400
Wet strength, kg/cm²	600	500	200	100	< 50
Water absorption, %	20	80	150	190	220
Biodegradability, days	5	4	3	1	1

Example 3.

The experimental procedure was substantially the same as in Example 1 in each of the experiments except that the amounts of chitosan and starch were always 20 parts and 100 parts, respectively, per 100 parts of the cellulose pulp and the temperature for drying and heat treatment of the slurry spread over a

metal dish was varied in the range from 30 to 200 °C. The results of the tests for dry wet strength, amount of water absorption and biodegradability of the films are shown in Table 3 below.

As is understood from the results shown in Table 3 the temperature of the heat treatment is a factor influencing the dry strength and biodegradability of the composite films. Namely, the temperature should be 50 °C or higher in order to provide a practically useful dry strength for the film without losing adequate biodegradability.

Table 3

Heat treatment at, °C	30	50	100	150	200
Dry strength, kg/cm²	300	800	1000	1100	1100
Wet strength, kg/cm²	50	100	200	210	210
Water absorption, %	-	150	130	110	90
Biodegradability, days	< 1	1	3	7	10

Claims

1. A water absorptive cellulose fiber-based composite material in the form of a shaped body which comprises:
(A) 100 Parts by weight of fine cellulose fibers;
(B) from 5 to 100 parts by weight of chitosan; and
(C) from 10 to 300 parts by weight of glutinized starch.

2. A method for the preparation of a cellulose fiber-based water absorptive composite material in the form of a shaped body which comprises the steps of:
(a) blending 100 parts by weight of fine cellulose fibers, an aqueous solution of a chitosan salt in an amount in the range from 5 to 100 parts by weight as chitosan and from 10 to 300 parts by weight of glutinized starch to give an aqueous slurry;
(b) shaping the aqueous slurry into a form; and
(c) drying the thus shaped form of the aqueous slurry by heating at a temperature in the range from 50 to 200 °C.

3. A method as claimed in Claim 2 wherein the chitosan salt is an acetate of chitosan.

4. A method as claimed in Claim 2 or Claim 3 wherein the fine cellulose fibers have a fineness of 50 ml or less of Canadian standard freeness.

5. A method as claimed in any one of Claims 2 to 4 wherein the degree of deacylation of the chitosan is at least 40%.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 2420

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	GB-A-2 050 459 (S. GASLAND) * Abstract * ---	1	C 08 L 1/02 C 08 L 3/02 C 08 J 5/04 // (C 08 L 1/02 C 08 L 5:08)
A	PATENT ABSTRACTS OF JAPAN, vol. 5, no. 12 (C-40)[684], 24th January 1981; & JP-A-55 141 171 (KURARAY K.K.) 04-11-1980 * Abstract * ---	1	
A	PATENT ABSTRACTS OF JAPAN, vol. 12, no. 270 (C-515)[3117], 27th July 1988; & JP-A-63 49 212 (TOYO ROSHI K.K.) 02-03-1988 * Abstract * ---	1	
A	US-A-4 099 976 (K. KRASKIN) * Column 2, lines 15-23 * ---		
A	CH-A- 657 370 (H. MUNTWYLER) * Page 3, lines 46-53 * ---		TECHNICAL FIELDS SEARCHED (Int. Cl.5)
P,A	EP-A-0 323 732 (JAPAN; DIRECTOR GENERAL OF AGENCY OF INDUSTRIAL SCIENCE AND TECHNOLOY) * Page 3, lines 35-38 * -----	1	C 08 L C 08 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-07-1990	SOMERVILLE F.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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